Claims

We claim:

1. A process of polymerizing olefins comprising contacting, in a reactor:

   (a) ethylene and at least one comonomer selected from the group consisting of C4 to C8 alpha olefins; and

   (b) a supported catalyst system comprising a metallocene catalyst compound activated by methylaluminoxane, and a support material, the methylaluminoxane being present in the range of from 3 to 9 mmole methylaluminoxane per gram of support material, the metallocene being present in the range of from 0.01 to 1.0 mmole metallocene per gram of support material;

   wherein the catalyst has an activity of at least 2,500 grams polyethylene per gram of catalyst compound per hour; and the process produces a polymer having a bulk density of at least 0.30 gram/cubic centimeter.

2. The process of claim 1 wherein the polymerization process is a gas phase process.

3. The process of claim 1 wherein the polymerization process is a slurry process.

4. The process of claim 1 wherein the support material is selected from the group consisting of silica, alumina, silica-alumina, magnesium chloride, graphite, and mixtures thereof.

5. The process of claim 1 wherein the metallocene catalyst compound is a substituted bis-cyclopentadienyl zirconocene catalyst compound comprising at least one fluoride or fluorine containing leaving group.

6. The process of claim 1 wherein the reactor demonstrates a Fouling Index in the range of less than or equal to 2.

7. The process of claim 6 wherein the methylaluminoxane is present in an amount in the range of from 4 to 7.7 mmole methylaluminoxane per gram of support material.

8. The process of claim 7 wherein the methylaluminoxane is present in an amount in the range of from 5 to 6.5 mmole methylaluminoxane per gram of support material.

9. The process of claim 8 wherein the methylaluminoxane is present in an amount in the range of from 6 to 6.5 mmole methylaluminoxane per gram of support material.

10. The process of claim 6 wherein the metallocene catalyst compound is present in an amount in the range of from 0.04 to 0.1 mmole metallocene per gram of support material.

11. The process of claim 10 wherein the metallocene catalyst compound is present in an amount in the range of from 0.05 to 0.08 mmole metallocene per gram of support material.

12. The process of claim 11 wherein the metallocene catalyst compound is present in an amount in the range of from 0.06 to 0.07 mmole metallocene per gram of support material.

13. The process of claim 1 wherein the catalyst has an activity of at least 5,000 grams polyethylene per gram of catalyst compound per hour.

14. The process of claim 13 wherein the catalyst has an activity of at least 7,500 grams polyethylene per gram of catalyst compound per hour.

15. The process of claim 6 wherein the Fouling Index is less than or equal to 1.

16. The process of claim 15 wherein the Fouling Index is 0.

17. The process of claim 1 wherein the polymer produced has a bulk density of at least 0.4 grams per cubic centimeter.

18. The process of claim 17 wherein the polymer produced has a bulk density of at least 0.48 grams per cubic centimeter.

19. The process of claim 1 wherein the metallocene catalyst compound is selected from the group consisting of: bis(1,3-methyl-n-butylcyclopentadienyl) zirconium difluoride; bis(n-propylcyclopentadienyl) zirconium difluoride; (tetramethyl

cyclopentadienyl) (n-propyl cyclopentadienyl) zirconium difluoride; and (pentamethyl cyclopentadienyl) (n-propyl cyclopentadienyl) zirconium difluoride.

20. The process of claim 1 wherein an antistatic agent is absent or substantially absent from the catalyst composition.

21. The process of claim 20 wherein the support material has a surface area in the range of from 150 to 450 m^2/gram.

22. The process of claim 20 wherein the support material has a pore volume in the range of from 1 to 2.5 cm^3/gram.

23. The process of claim 20 wherein the support material has an average particle size in the range of from 10 to 50 μm.

24. The process of claim 1 wherein an antistatic agent is present in the catalyst composition in an amount less than 4 % by weight of the catalyst composition.

25. The process of claim 24 wherein the antistatic agent is present in the catalyst composition in an amount in the range of from 0 % to 2 % by weight of the catalyst composition.

26. The process of claim 1 wherein the support material has a surface area in the range of from 150 to 450 m^2/gram.

27. The process of claim 26 wherein the support material has a surface area in the range of from 250 to 400 m^2/gram.

28. The process of claim 27 wherein the support material has a surface area in the range of from 300 to 350 m^2/gram.

29. The process of claim 1 wherein the support material has a pore volume in the range of from 1 to 2.5 cm^3/gram.

30. The process of claim 29 wherein the support material has a pore volume in the range of from 1.25 to 2.0 cm^3/gram.

31. The process of claim 30 wherein the support material has a pore volume in the range of from 1.5 to 1.75 cm^3/gram.

32. The process of claim 1 wherein the support material has an average particle size in the range of from 10 to 50 μm.

33. The process of claim 32 wherein the support material has an average particle size in the range of from 15 to 40 μm.

34. The process of claim 33 wherein the support material has an average particle size of from 20 to 30 μm.

35. A supported catalyst system comprising a metallocene catalyst compound activated by methylaluminoxane, and a support material, the methylaluminoxane being present in the range of from 3 to 9 mmole methylaluminoxane per gram of support material, the metallocene being present in the range of from 0.01 to 1.0 mmole metallocene per gram of support material.

36. The supported catalyst system of claim 35 wherein the metallocene catalyst compound is represented by a formula selected from the group consisting of:

$Cp^ACp^BMX_n$;

$Cp^A(A)Cp^BMX_n$;

$Cp^A(A)QMX_r$;

$Cp^AMQ_qX_w$;

$Cp^AM(W_2GZ)X_y$; and

$T(Cp^AM(W_2GZ)X_y)_m$

wherein M is a metal atom selected from the group consisting of: Group 3 to Group 12 metal atoms;

Cp is a ligand selected from the group consisting of: substituted or unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl;

X is selected from the group consisting of: halogen ions, hydrides, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12} alkoxys, C_6 to C_{16} aryloxys, C_7 to C_{18} alkylaryloxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, C_1 to C_{12} heteroatom-containing hydrocarbons and substituted derivatives thereof; amines, phosphines, ethers, carboxylates, dienes, and hydrocarbon radicals having from 1 to 20 carbon atoms;

(A) is a bridging group;

Q is a heteroatom-containing ligand;

T is a bridging group selected from the group consisting of C_1 to C_{10} alkylenes, C_6 to C_{12} arylenes and C_1 to C_{10} heteroatom containing groups, and C_6 to C_{12} heterocyclic groups;

G is selected from the group consisting of carbon and silicon;

W is selected from the group consisting of –O-; -NR-; $-CR_2-$ and –S-;

R is selected from the group consisting of C_1 to C_{10} heteroatom containing groups, C_1 to C_{10} alkyls, C_6 to C_{12} aryls, C_6 to C_{12} alkylaryls, C_1 to C_{10} alkoxys, and C_6 to C_{12} aryloxys;

Z is selected from the group consisting of of R, –OR, $–NR_2$, $–CR_3$, –SR, $–SiR_3$, $–PR_2$, and hydride;

each X is chemically bonded to M;

each Cp group is chemically bonded to M;

m is an integer in the range of from 1 to 7;

n is 0 or an integer from 1 to 4;

q is in the range of from 0 to 3;

r is 0, 1 or 2;

w is in the range of from 0 to 3; and

y is 1 or 2.

37. The supported catalyst system of claim 36 wherein the methylaluminoxane is present in an amount in the range of from 4 to 7.7 mmole methylaluminoxane per gram of support material.

38. The supported catalyst system of claim 37 wherein the methylaluminoxane is present in an amount in the range of from 5 to 6.5 mmole methylaluminoxane per gram of support material.

39. The supported catalyst system of claim 38 wherein the methylaluminoxane is present in an amount in the range of from 6 to 6.5 mmole methylaluminoxane per gram of support material.

40. The supported catalyst system of claim 36 wherein the metallocene catalyst compound is present in an amount in the range of from 0.04 to 0.1 mmole metallocene per gram of support material.

41. The supported catalyst system of claim 37 wherein the metallocene catalyst compound is present in an amount in the range of from 0.05 to 0.08 mmole metallocene per gram of support material.

42. The supported catalyst system of claim 38 wherein the metallocene catalyst compound is present in an amount in the range of from 0.06 to 0.07 mmole metallocene per gram of support material.

43. The supported catalyst system of claim 36 wherein an antistatic agent is absent or substantially absent from the catalyst composition.

44. The supported catalyst system of claim 43 wherein the support material has a surface area in the range of from 150 to 450 m^2/gram.

45. The supported catalyst system of claim 43 wherein the support material has a pore volume in the range of from 1 to 2.5 cm^3/gram.

46. The supported catalyst system of claim 43 wherein the support material has an average particle size in the range of from 10 to 50 μm.

47. The supported catalyst system of claim 36 wherein an antistatic agent is present in the catalyst composition in an amount less than 4 % by weight of the catalyst composition.

48. The supported catalyst system of claim 47 wherein the antistatic agent is present in the catalyst composition in an amount in the range of from 0 % to 2 % by weight of the catalyst composition.

49. The supported catalyst system of claim 36 wherein the support material has a surface area in the range of from 150 to 450 m^2/gram.

50. The supported catalyst system of claim 49 wherein the support material has a surface area in the range of from 250 to 400 m^2/gram.

51. The supported catalyst system of claim 50 wherein the support material has a surface area in the range of from 300 to 350 m^2/gram.

52. The supported catalyst system of claim 36 wherein the support material has a pore volume in the range of from 1 to 2.5 cm^3/gram.

53. The supported catalyst system of claim 52 wherein the support material has a pore volume in the range of from 1.25 to 2.0 cm^3/gram.

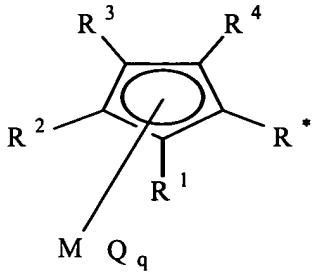
54. The supported catalyst system of claim 53 wherein the support material has a pore volume in the range of from 1.5 to 1.75 cm^3/gram.

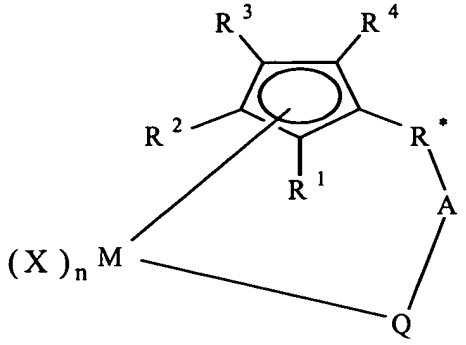
55. The supported catalyst system of claim 36 wherein the support material has an average particle size in the range of from 10 to 50 μm.

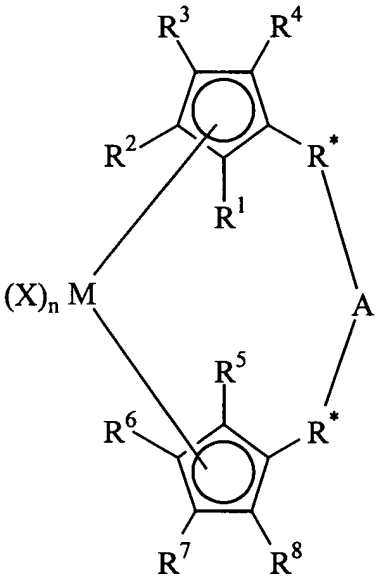
56. The supported catalyst system of claim 55 wherein the support material has an average particle size in the range of from 15 to 40 μm.

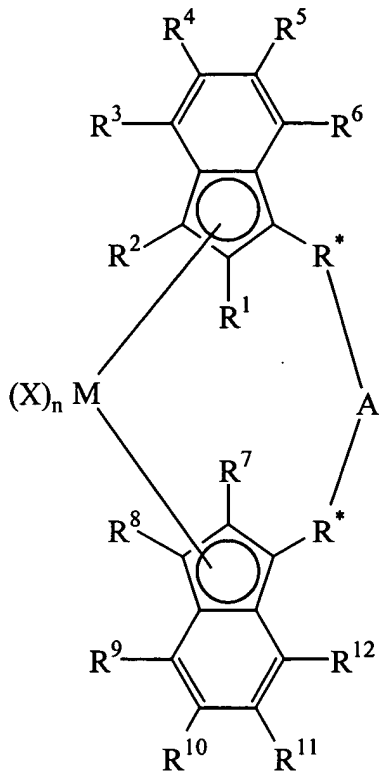
57. The supported catalyst system of claim 56 wherein the support material has an average particle size of from 20 to 30 μm.

58. The supported catalyst system of claim 35 wherein the metallocene catalyst compound is represented by a formula selected from the group consisting of:

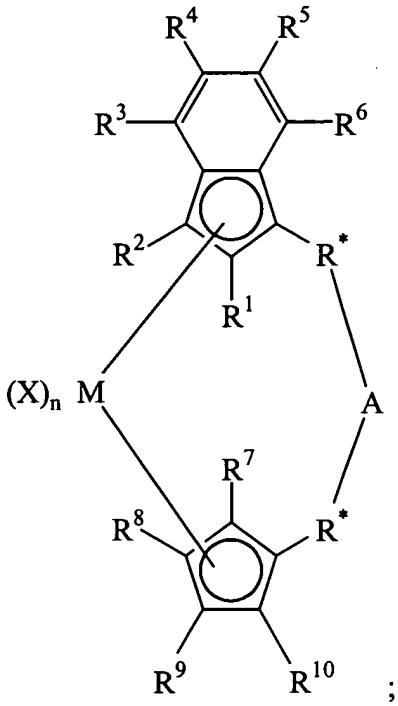








and



;

wherein M is a metal atom selected from the group consisting of: Group 3 to Group 12 metal atoms;

Q in (Va-i) and (Va-ii) is selected from the group consisting of halogen ions, alkyls, alkylenes, aryls, arylenes, alkoxys, aryloxys, amines, alkylamines, phosphines, alkylphosphines, substituted alkyls, substituted aryls, substituted alkoxys, substituted aryloxys, substituted amines, substituted alkylamines, substituted phosphines, substituted alkylphosphines, carbamates, heteroallyls, carboxylates (non-limiting examples of suitable carbamates and carboxylates include trimethylacetate, trimethylacetate, methylacetate, p-toluate, benzoate, diethylcarbamate, and dimethylcarbamate), fluorinated alkyls, fluorinated aryls, and fluorinated alkylcarboxylates;

q is an integer ranging from 1 to 3;

each R^* is independently selected from the group consisting of hydrocarbyls and heteroatom-containing hydrocarbyls;

A is a bridging group;

X is selected from the group consisting of: halogen ions, hydrides, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12} alkoxys, C_6 to C_{16} aryloxys, C_7 to C_{18} alkylaryloxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, C_1 to C_{12} heteroatom-containing hydrocarbons and substituted derivatives thereof; amines, phosphines, ethers, carboxylates, dienes, and hydrocarbon radicals having from 1 to 20 carbon atoms;

n is 0 or an integer from 1 to 4; and

R^1 through R^{12} are independently: selected from the group consisting of hydrogen radical, halogen radicals, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12} alkoxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, and C_1 to C_{12} heteroatom-containing hydrocarbons and substituted derivatives thereof.

59. The supported catalyst system of claim 58 wherein the methylaluminoxane is present in an amount in the range of from 4 to 7.7 mmole methylaluminoxane per gram of support material.

60. The supported catalyst system of claim 59 wherein the methylaluminoxane is present in an amount in the range of from 5 to 6.5 mmole methylaluminoxane per gram of support material.

61. The supported catalyst system of claim 60 wherein the methylaluminoxane is present in an amount in the range of from 6 to 6.5 mmole methylaluminoxane per gram of support material.

62. The supported catalyst system of claim 58 wherein the metallocene catalyst compound is present in an amount in the range of from 0.04 to 0.1 mmole metallocene per gram of support material.

63. The supported catalyst system of claim 62 wherein the metallocene catalyst compound is present in an amount in the range of from 0.05 to 0.08 mmole metallocene per gram of support material.

64. The supported catalyst system of claim 63 wherein the metallocene catalyst compound is present in an amount in the range of from 0.06 to 0.07 mmole metallocene per gram of support material.

65. The supported catalyst system of claim 58 wherein an antistatic agent is absent or substantially absent from the catalyst composition.

66. The supported catalyst system of claim 65 wherein the support material has a surface area in the range of from 150 to 450 m^2/gram.

67. The supported catalyst system of claim 65 wherein the support material has a pore volume in the range of from 1 to 2.5 cm^3/gram.

68. The supported catalyst system of claim 65 wherein the support material has an average particle size in the range of from 10 to 50 μm.

69. The supported catalyst system of claim 58 wherein an antistatic agent is present in the catalyst composition in an amount less than 4 % by weight of the catalyst composition.

70. The supported catalyst system of claim 66 wherein the antistatic agent is present in the catalyst composition in an amount in the range of from 0 % to 2 % by weight of the catalyst composition.

71. The supported catalyst system of claim 58 wherein the support material has a surface area in the range of from 150 to 450 m^2/gram.

72. The supported catalyst system of claim 71 wherein the support material has a surface area in the range of from 250 to 400 m^2/gram.

73. The supported catalyst system of claim 72 wherein the support material has a surface area in the range of from 300 to 350 m^2/gram.

74. The supported catalyst system of claim 58 wherein the support material has a pore volume in the range of from 1 to 2.5 cm^3/gram.

75. The supported catalyst system of claim 74 wherein the support material has a pore volume in the range of from 1.25 to 2.0 cm^3/gram.

76. The supported catalyst system of claim 75 wherein the support material has a pore volume in the range of from 1.5 to 1.75 cm^3/gram.

77. The supported catalyst system of claim 58 wherein the support material has an average particle size in the range of from 10 to 50 μm.

78. The supported catalyst system of claim 77 wherein the support material has an average particle size in the range of from 15 to 40 μm.

79. The supported catalyst system of claim 78 wherein the support material has an average particle size of from 20 to 30 μm.